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MODEL ADHEREND SURFACE EFFECTS ON EPOXY CURE REACTIONS

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ABSTRACT

Adherend surface effects on the amine cure of epoxy resins were investigated using finely divided aluminum oxide as high surface area models for aluminum. Calorimetric analysis of simplified crosslinking systems revealed significantly faster reactions which led to lower glass transition temperature materials for activated aluminum oxide filled samples. A monofunctional amine and epoxy were then utilized to obtain soluble reaction products amenable to molecular characterization. These studies similarly showed an increase in the rate of epoxy consumption in the presence of activated aluminum oxide which was attributed to both an increase in the rate of amine addition to epoxy, as well as to epoxy homopolymerization. The latter was not observed in the unfilled mixtures. Such changes in reaction mechanism at the adherend surface have implications for the strength and durability of actual adhesive bonds.

CONTENTS

INTRODUCTION

For the past several years, the U.S. Army has been engaged in a major effort to improve the quality of adhesively bonded joints in a broad range of materiel.[1] This effort involves both short-term problem solving and long-term research in adhesion science. As part of this latter effort, in recognition of the critical role of the "interphase" in controlling the performance of adhesive bonds,[2,3] we have been studying the effect of adherend surfaces on adhesive cure chemistry. Our objective is a description, at the molecular level, of the structure of this region in support of ongoing efforts to construct predictive models of bonded joint strength and service life.

One of the first indications that an adherend surface might perturb the cure chemistry of and epoxy adhesive is the work of Comyn et al.[4] Through the use of inelastic electron tunneling spectroscopy, it was concluded that no cure took place in the interphase due to preferential amine adsorption onto the aluminum oxide surface of an aluminum adherend.

Dillingham and Boerio[5] studied the interaction of an amine-cured epoxy with a polished aluminum surface by means of X-ray photoelectro spectroscopy and reflection absorption infrared spectroscopy. They concluded that the catalytic action of the acidic hydroxyl groups on the aluminum oxide surface led to a cured resin with a higher crosslink density in this interphase. They inferred that the resultant increased brittleness was responsible for the failure which was observed to occur in this region.

Similarly, Garton et al.[6] have studied the effect of various carbon and carbon fiber surfaces on the course of and epoxy/amine reaction. Using thermal analysis and infrared spectroscopy, they determined that an acidic carbon surface (produced by oxidation) resulted in selective amine adsorption and the catalytic acceleration of its reaction with the epoxy.

Using transmission electron microscopy, Crompton[7] observed that the appearance of a cured epoxy adhesive in contact with an aluminum adherend differed from that in the bulk. A lower density material at the surface was evidenced by a higher electron transparency. It was further observed that the apparent adhesive failure of this joint was actually cohesive failure in this very thin "transition region".

Most recently, Nigro and Ishida[8] used infrared spectroscopy to show that a polished automotive steel catalyzed the homopolymerization of an epoxy resin at the surface.

Although sometimes contradictory, results of these various studies clearly indicate an effect of adherend surfaces on cure chemistry. However, all make use of less than absolute methods to determine the structure of the cured adhesives in contact with these surfaces. We have undertaken an alternative approach to the investigation of this problem. Simplified crosslinking adhesive systems were first investigated, and then a monofunctional amine and epoxy were utilized in

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2. SHARPE, L. H. J. Adhesion, v. 29, 1989, p. 1.
3. National Materials Advisory Board, Reliability of Adhesive Bonds under Severe Environments, NMAB-422, 1984, p. 31-34.
4. COMYN, J., HORLEY, C. C., OXLEY, D. P., PRITCHARD, R. G., and TEGG, J. L. J. Adhesion, v. 12, 1981, p. 171.
5. DILLINGHAM, R. G., and BOERIO, F. J. J. Adhesion, v. 24, 1987, p. 315.
6. GARTON, A., STEVENSON, W. T. K., and WANG, S. P. J. Polym. Sci. Chem. Ed., v. 26, 1988, p. 1377.
7. CROMPTON, J. S. J. Mater. Sci., v. 24, 1989, p. 1575.
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order to obtain soluble products amenable to molecular characterization by conventional analytical techniques. Both the crosslinking and model systems were used in conjunction with finely divided aluminum oxides which serve as high surface area models of aluminum adherend surfaces. Some of the initial results of this effort are the subject of this report.

EXPERIMENTAL

The epoxy resins used in this study consisted of Epon 826, a diglycidyl ether of bisphenol A (DGEBA) resin (Shell Chemical Company), and the monofunctional glycidyl ether of cumyl phenol (MGECP). The 826 was used as received. MGECP was prepared by the reaction of the sodium salt of cumyl phenol with an excess of epichlorohydrin followed by vacuum distillation of the crude product. MGECP is a clear liquid at room temperature with a purity of greater than 99% by high performance liquid chromatography (HPLC).

The curing agents used include the primary aromatic diamines 3,3'-diaminodiphenyl sulfone (3,3'-DDS) and 4,4'-diaminodiphenyl sulfone (4,4'-DDS) (Aldrich Chemical Company) and the primary aromatic amine 4-aminodiphenyl sulfone (ADS).[9] The purity of the curing agents was determined to be greater than 99% by HPLC.

Fillers employed in the differential scanning calorimetry (DSC) studies were an activated/neutral alumina, a fused alumina, and powdered aluminum. Fillers for all the additional experiments were a series of aluminum oxides from Aldrich Chemical Company: activated acidic (A/A), activated neutral (A/N), activated basic (A/B) (all Brockmann I grade), and corundum (crystalline, α-form). The activated aluminas have a surface area of approximately 155 m^2/g with a pore size of 58Å at 150 mesh. The corundum was 60 to 200 mesh.

Resin formulations were mixed at room temperature and stored at -18^oC if not used immediately. The aluminum oxide of interest was admixed with the resin immediately prior to cure. Approximately 0.5 g of a filled mixture was prepared from which aliquots for further testing were taken.

DSC analyses were carried out on 10 to 30 mg samples encapsulated in O-ring sealed stainless steel sample containers. Dynamic DSC experiments were performed on Perkin-Elmer DSC-2C equipped with an intercooler. Dynamic cures were carried out at either 2.5^{o}C/min or 5°C/min followed by a second scan at the same heating rate to establish a baseline and a final scan at 20°C/min for the glass transition temperature (T_g) determination. All scans were made from 27°C to 277°C (300°K to 550°K). Isothermal DSC experiments were performed on a Perkin-Elmer DSC-2 equipped with a constant temperature water bath. Samples were heated at 320°C/min to the isothermal cure temperature and the heat flow monitored on a strip chart recorder until the response leveled to a constant baseline. This was followed by two heating scans at 20°C/min from 27°C to 277°C. The T_g was determined from the second scan. The reported T_g's of both the dynamic and isothermally cured samples were from the midpoint of the heat capacity change.

Torsional braid analysis (TBA) of the unfilled samples was carried out on an automated TBA system from Plastics Analysis Instruments, Inc. A glass braid was wetted with a

9 ZUKAS, W. X., DUNN, D. A., and GILBERT, M. D Proc. ACS Div. Polym. Mat. Sci. Eng., v. 56, 1987, p. 316.

methylene chloride solution of the resin formulation, the solvent allowed to evaporate, and the impregnated braid introduced into a preheated sample chamber. The peaks in the log decrement trace associated with the gelation and vitrification times were recorded. TBA was found not to be useful for filled systems. Only resin penetrated the braid leaving filler on the outer surface.

HPLC analyses were carried out on a Waters Associates Model ALC/GPC 244 Chromatograph with a WISP 710B injector and a Lambda-Max Model 481 LC Spectrophotometer at 214 nm. Samples for HPLC analyses were isothermally cured in either stainless steel DSC pans or glass vials. Samples were then dissolved in an appropriate solvent and passed through a 0.2 μm filter and analyzed using a Waters Nova-Pak C18 reverse phase column with an acetonitrile/water mobile phase. Five μL of a 0.1% sample solution was injected for analysis.

Thermogravimetric analysis (TGA) was run on a Dupont 9900 Thermal Analyzer and a 951 TGA module. Runs were made on 5 to 15 mg of sample at 20°C/min in flowing air at 100cc/min.

Mass spectra were obtained using a Hewlett-Packard HP 5996A quadrupole mass spectrometer operating at an electron ionization of 70 ev. Both a direct insertion probe technique and pyrolysis gas chromatography/mass spectrometry were employed. Mass spectra were generally obtained on samples heated at 10°C/min from 30°C to approximately 320°C.

Fourier transform Raman (FTR) spectra were obtained on a Spex FT R/IR spectrometer with an Nd/YAG laser at 1064 nm at approximately one watt.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

RESULTS AND DISCUSSION

The amine cure of epoxy resins generally proceeds through the following reactions:

$$-CH_2-CH-CH_2 + NH_2-R \longrightarrow -CH_2-CH-CH_2-NH-R$$

$$-CH_2-CH-CH_2 + NH-R_1 \longrightarrow -CH_2-CH-CH_2-N \backslash R_2$$

$$-CH_2-CH-CH_2 + HO-R \longrightarrow -CH_2-CH-CH_2-O-R$$
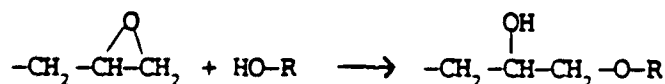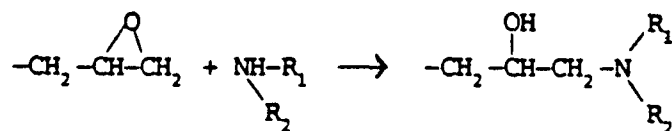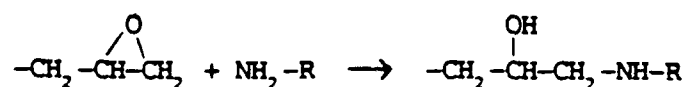
The reactions represent primary amine addition to epoxy, secondary amine addition to epoxy, and subsequent homopolymerization, respectively. Shechter et al.[10,11] found the first two reactions to dominate the cure of a glycidyl ether epoxy with aliphatic amines. For a similar system Dusek et al.[12] arrived at the same conclusion, but found the third reaction to take place in the presence of excess epoxy. Anderson[13] also found a significant amount of homopolymerization to take place when glycidyl ether epoxies were cured with aliphatic amines. However, when an aromatic amine was used, the amount of homopolymerization became negligible. It was thought that the tertiary aromatic amine which is formed in the second reaction was too sterically hindered to have any catalytic effect on the third reaction. Bell[14] and Byrne et al.[15] also found that no homopolymerization took place in the cure of glycidyl ether epoxies with aromatic amines.

Each of the above three reactions has been reported[16] to release the same molar heat of reaction. DSC measurements can thus be related to the extent of reaction of the epoxy groups and can be used to study the kinetics of cure, providing the total heat of reaction remains constant. The 3,3'-DDS was initially selected since it provided a system which was relatively unreactive at room temperature yet reactive enough to complete cure below 277°C in dynamic DSC experiments, thus avoiding degradation. Different heating rates were also employed to keep the complete exotherm below 277°C. Use of the more conventional 4,4'-DDS was first attempted in dynamic experiments, but discontinued when complete cure could not be obtained below this temperature.

The dynamic DSC results for the various 826/3,3)-DDS mixtures are shown in Table 1. Addition of activated aluminum oxide was found to lower the exotherm peak temperature and decrease the T_g of the resulting cured material with higher filler loading levels leading to lower T_g's. These effects were observed for different heating rates and for different epoxy/amine ratios. The dynamic scans of a stoichiometric mixture of 826/3,3'-DDS are shown in Figures 1a and 1b for an unfilled sample and a 100 parts per hundred resin by weight (phr) activated aluminum oxide filled sample, respectively. The large shifts in the exotherm position and shape are obvious. Neither of these effects were observed for the aluminum or fused alumina filled samples.

The heat of reaction values were calculated from the peak area defined by a straight baseline for the first heating curve added to the area defined by the same limits for the second heating scan. This procedure was used to minimize the effects of baseline curvature. An essentially constant value for heat of reaction is shown in Table 1 for the unfilled and activated aluminum oxide filled stoichiometric samples heated at 5°C/min. However, the same sample series at 2.5°C/min shows a decreasing heat of reaction with increasing filler level. Also, the aluminum and fused alumina filled samples show a higher heat of reaction than that of the other samples at 5°C/min. These discrepancies were attributed to over 200°C wide baselines used to define the exotherm (see Figure 1b). Such variation in the total heat of reaction precluded the use of dynamic DSC for the determination of the extent of reaction.

Although not useful for kinetic studies, the dynamic DSC clearly indicated that activated aluminum oxide had a significant effect on the course of the cure process for the 826/3,3'-DDS system as evidenced by changes in both the cure exotherm profile and the T_g of the resulting cured

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11. SHECHTER, L., WYNSTRA, J., and KURKJY, R. P. Ind. Eng. Chem., v. 48, 1956, p. 94.
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16. HAGNAUER, G. L., PEARCE, P. J., LALIBERTE, B. R., and ROYLANCE, M. E. ACS Symp. Ser. v. 227, 1983, p. 25

product. To obtain data more amenable to kinetic analysis, as well as to avoid possible degradation at high temperatures, isothermal DSC experiments were undertaken.

Table 1. DYNAMIC DSC RESULTS FOR 826/3,3)-DDS

Sample	Exotherm Peak T(°C)	Heat of Rxn J/g-resin	Tg(°C)
Epoxy/Amine 1/1 (5°C/min)			
Unfilled	191	396	156
50 phr Aluminum	187	514	160
25 phr Activated Al₂O₃	187	389	147
50 phr Activated Al₂O₃	181	395	141
100 phr Activated Al₂O₃	168	393	130
50 phr Fused Alumina	192	478	160
Epoxy/Amine 1/1 (2.5°C/min)			
Unfilled	176	485	166
25 phr Activated Al₂O₃	169	439	154
50 phr Activated Al₂O₃	154	353	139
100 phr Activated Al₂O₃	151	321	136
Epoxy/Amine 1.5/1 (2.5°C/min)			
Unfilled	184	348	134
50 phr Activated Al₂O₃	172	350	118

The isothermal DSC studies were carried out between 120°C to 210°C for unfilled stoichiometric mixtures of 826/3,3'-DDS and 826/4,4'-DDS and between 100°C to 160°C for the same mixtures filled with 50 phr activated aluminum oxide. Figure 2 shows the heat flow versus time for isothermal cures of 826/4,4'-DDS, both unfilled and filled at 140°C. A much faster initial rate of reaction was observed for the filled samples at all comparable cure temperatures. Garton et al.[6] similarly observed an acceleration of epoxy-primary amine reaction in the initial stages of cure when an air oxidized crushed carbon fiber was used as a filler.

The average heat of reaction values from the isothermal DSC experiments are listed in Table 2. These values were observed to be essentially the same at approximately 480 J/g for all the mixtures investigated, independent of the presence of filler or type of curing agent. This value is higher than that reported by other investigators of similar systems. Heat of reaction for stoichiometric mixtures of DGEBA resins with 4,4'-DDS have been reported at 325 J/g[17] for the average of a number of dynamic scanning rates, 389 J/g[18] for a scanning rate of 2.5°C/min, and 426 J/g[19] for a scanning rate of 10°C/min. However, all of these were obtained by dynamic DSC. The isothermal baseline is believed to lead to a more accurate and consistent value of the heat of reaction and accounts for the discrepancy between our results and those previously reported.

17. BARTON, J. M. Polymer., v. 21, 1980, p. 603.
18. GALY, J., SABRA, A., and PASCAULT, J. P. Polym. Eng. Sci., v. 26, 1986, p. 1514.
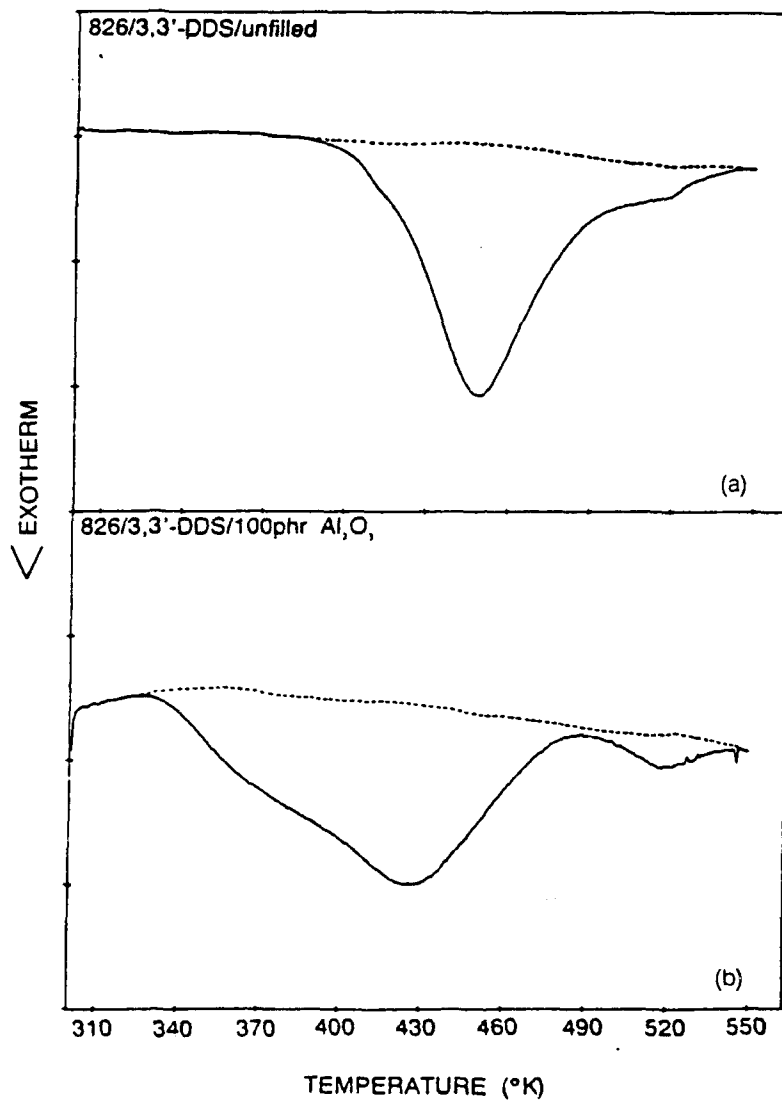19. RICCARDI, C. C., and WILLIAMS, R. J. J. J. Appl. Polym. Sci., v. 32, 1986, p. 3445.

Figure 1. Dynamic DSC traces at 2.5°C/min for a stoichiometric
826/3,3′−DDS (a) unfilled mixture and (b) 100 phr activated
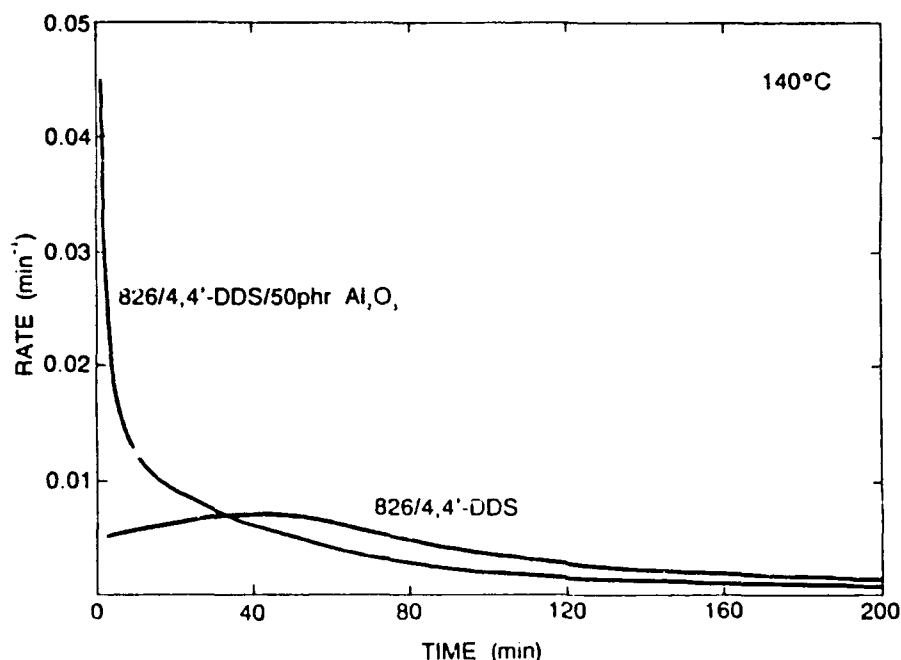aluminum oxide filled mixture.

Figure 2. Isothermal DSC traces at 140°C for an unfilled and a 50 phr activated
aluminum oxide filled 826/4,4'-DDS stoichiometric mixture.

Table 2. ISOTHEP***L HEAT OF REACTION AND
GLASS TRANSITION TEMPERATURES

Sample	J/g-resin	Tg(°C)
826/3,3)-DDS	476	155
826/3,3)-DDS/50 phr Activated Al₂O₃	478	149
826/4,4)-DDS	478	187
826/4,4)-DDS/50 phr Activated Al₂O₃	483	159

Table 2 also shows the T_g values obtained for these resin systems. The T_g of 187°C for
e 826/4,4'-DDS unfilled resin is in good agreement with the 189°C and 190°C reported by
hers.[17,18] Inclusion of the filler lowered the T_g of the 3,3'-DDS resin by approximately
C, but had a greater effect on the 4,4'-DDS system, lowering the T_g by almost 30°C.
lthough the final extent of reaction appears to be the same for the filled and unfilled sys-
ms, as evidenced by the same total heat of reaction, the lower T_g's indicate a lower cross-
ik density for the filled systems. This is consistent with the lower T_g observed by Garton
al.[6] for the effect of an acidic carbon black surface and the lower density material
served by Crompton[7] next to an aluminum adherend surface. Garton attributed the lower
to a reduced final extent of reaction due to the absorption of amine at the surface.

Significant differences were not observed for the heat of reaction values obtained for the
wer cure temperatures compared to higher ones. Additionally, the first dynamic scan of the

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isothermally cured material did not show an exotherm due to additional reaction, although slight increases in T_g were observed for the second scan of samples initially cured at lower temperatures. This was somewhat surprising since the reported T_g values and the TBA results indicate that vitrification takes place during the lower temperature cures, which was expected to lead to cessation of reaction. The isothermal experiments were typically run for approximately 24 hours before the baseline was considered established, apparently allowing for essentially complete reaction even at these lower cure temperatures.

Since the total heat of a reaction appears to be constant, it is assumed that the extent of reaction is proportional to the partial heat of reaction and the rate of reaction is proportional to the rate of heat evolution. Plots of the rate of reaction versus extent of reaction for the isothermal cure of a filled and unfilled 826/3,3'-DDS and 826/4,4'-DDS samples at 130°C are shown in Figure 3. Both resin mixtures exhibit an accelerated initial rate of reaction for the filled samples with the 3,3'-DDS somewhat faster that the 4,4'-DDS. The unfilled samples show the typical autoaccelerated behavior associated with uncatalyzed epoxy/amine mixtures with a maximum rate of reaction at some extent of reaction greater than zero.
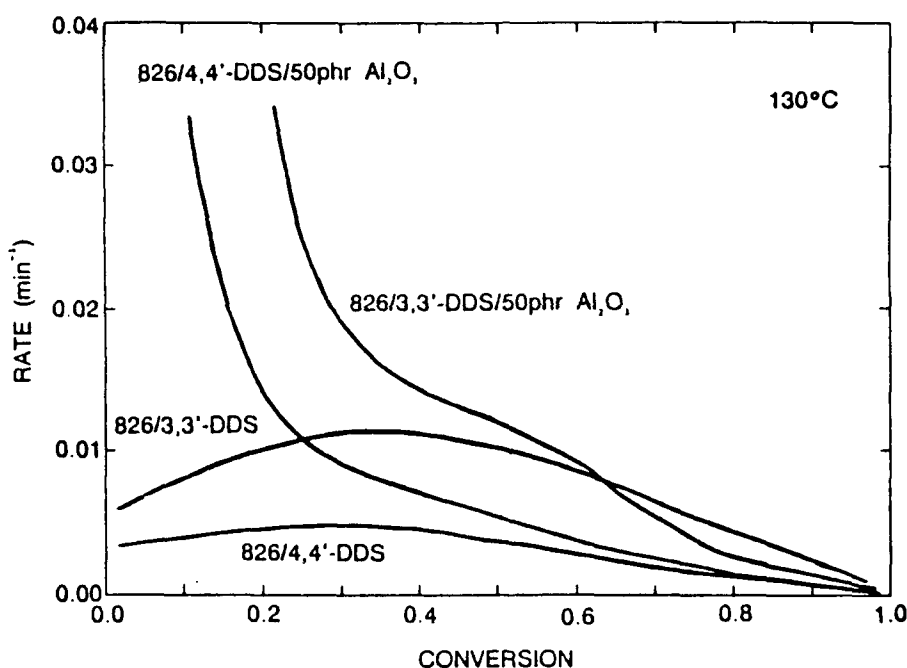
Figure 3. Isothermal rate versus extent of reaction traces from DSC at 140°C for unfilled and 50 phr activated aluminum oxide filled stoichiometric resin mixtures.

Activation energies were derived from plots of the natural logarithm of time to a particular extent of reaction (inversely proportional to the rate) versus the reciprocal of the isothermal cure temperature. These Arrhenius plots were made for unfilled and filled resin mixtures at 10%, 30%, and 50% extent if reaction and are shown in Figure 4 for the 30% curves. Values for the activation energies derived from these ، rves and from the gelation data for the unfilled resins by TBA are listed in Table 3. Accurate activation energy determination for the 10% curves of the filled systems was found to be difficult due to the very high initial rate of reaction. Otherwise, the resins generally show a gradually decreasing activation energy

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with extent of reaction. The values for the 4,4'-DDS mixtures are also slightly higher when compared to the corresponding 3.3'-DDS mixture. Gelation times by TBA were observed at 60% to 65% extent of reaction for both systems and result in similar activation energies. These values correspond well with the 63 kJ/mole reported by Galy et al.[18] from DSC studies of a DGEBA/4,4'-DDS mixture.

Table 3. ACTIVATION ENERGIES (kJ/MOLE) FROM ISOTHERMAL DSC AND TBA

Sample	10%	30%	50%	Gelation
826/3,3)-DDS	60	56	53	58
826/3,3)-DDS/50 phr Activated Al_2O_3	57	65	60	-
826/4,4)-DDS	64	62	60	61
826/4,4)-DDS/50 phr Activated Al_2O_3	54	73	71	-
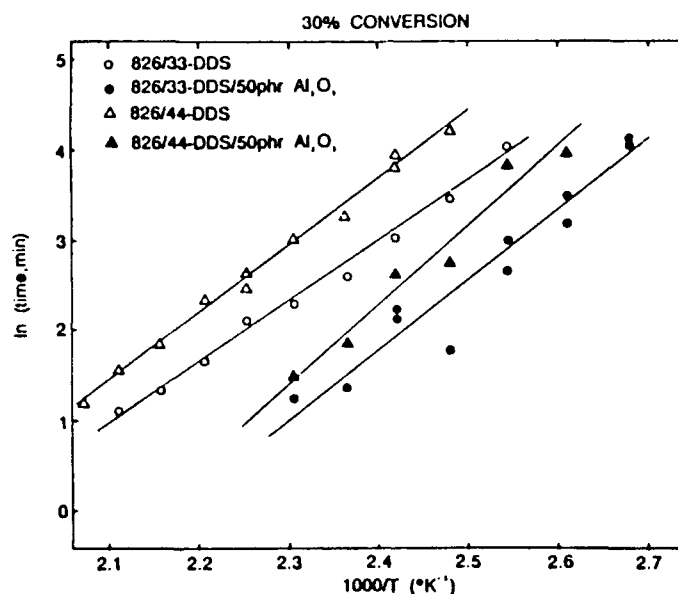
Figure 4. Arrhenius plots from 30% extent of reaction data from isothermal DSC experiments.

Overall, only relatively small differences were observed in the activation energies when comparing similar extents of reaction for filled and unfilled systems. Although a much faster initial reaction rate was observed for the activated aluminum oxide containing samples, its temperature dependence was similar to the unfilled resin. Riccardi et al.[20] attributed activation energies of 54 to 59 kJ/mole for DGEBA resins cured with ethylene diamine to the catalytic effect of the hydroxyl groups generated in the reaction. The increase in reaction rate observed in this study may thus be similarly due to the presence of catalytic sites, possibly hydroxylic, on the aluminum oxide surface. The change in T_g from unfilled to filled systems implies that the relative rates of the various network forming reactions are affected differently by the aluminum oxide surface.

20. RICCARDI, C. C., ADABBO, H. E., and WILLIAMS, R. J. J. J. Appl. Polym. Sci., v. 29, 1984, p. 2481.

Since DSC techniques provide no information as to the products of the various reactions, an alternate approach utilizing monofunctional model compounds was employed for this purpose. Stoichiometric mixtures of MGECP with ADS were investigated using HPLC. The
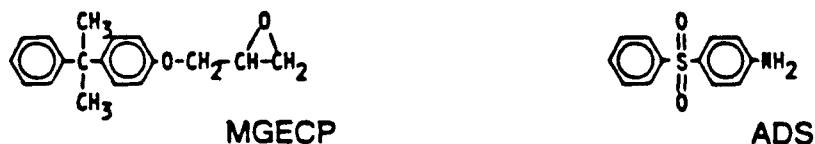
MGECP   ADS

HPLC traces of a typical reaction mixture of MGECP/ADS are shown in Figures 5a, 5b, and 5c after 0, 100, and 400 min at 160°C, respectively. As in previous work on an unfilled monofunctional epoxy with ADS,[9] these clearly show the formation of the primary amine addition product (1:1) followed by the formation of the diasteriomeric secondary amine addition products (2:1). While other minor peaks are observed in Figure 5c, the dominant reactions are amine addition to epoxy in the unfilled stoichiometric mixture.

ELUTION TIME (min)
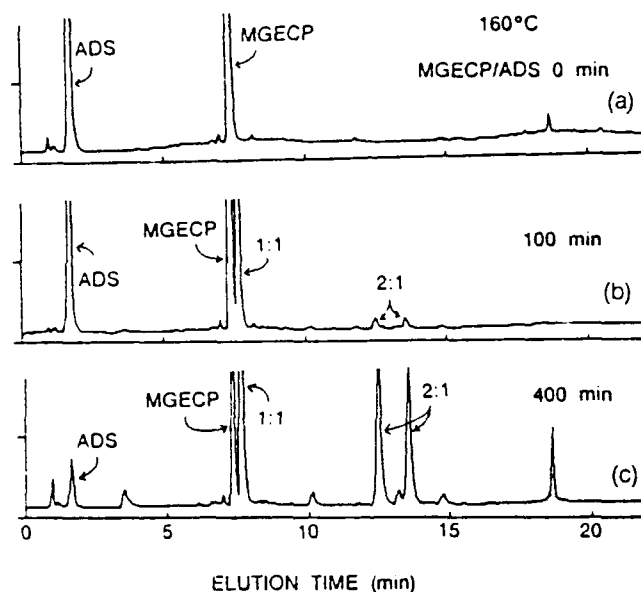
Figure 5. HPLC traces for an unfilled stoichiometric MGECP/ADS mixture heated at 160°C for (a) 0 minutes, (b) 100 minutes, and (c) 400 minutes.

Figures 6a, 6b, 6c, 6d, and 6e show the HPLC traces for an unfilled stoichiometric mixture and the same mixture filled with 50 phr corundum, 50 phr A/A, 50 phr A/N, and 50 phr A/B aluminum oxides, respectively, heated for 25 min at 160°C. The addition of corundum to the resin mixture appears to have no effect on the product distribution. A significant difference is observed when the activated aluminum oxides are added. More 1:1 product is produced in the same amount of time and an additional major reaction product is formed with an elution time of approximately 10 min. The HPLC traces of an unfilled and 50 phr A/N aluminum oxide filled samples heated for 200 min at 180°C are shown in Figures 7a and 7b, respectively. The same major reaction product with an elution time of 10 min is seen in Figure 7b, as observed in Figures 6c, 6d, and 6e, but no MGECP and a significant amount of ADS remain in the reactant

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mixture. At this point, it was speculated that this new product is the result of a reaction in which the amine does not participate. Additional heating of this sample produced no further change in the product distribution since no epoxy remains. This then represents the fully "cured" sample for these conditions. The activated aluminas thus lead to and acceleration of the epoxy/amine reactions and an entirely different reaction route, perhaps involving only the epoxy compound, leaving an excess of unreacted amine in a filled stoichiometric mixture.
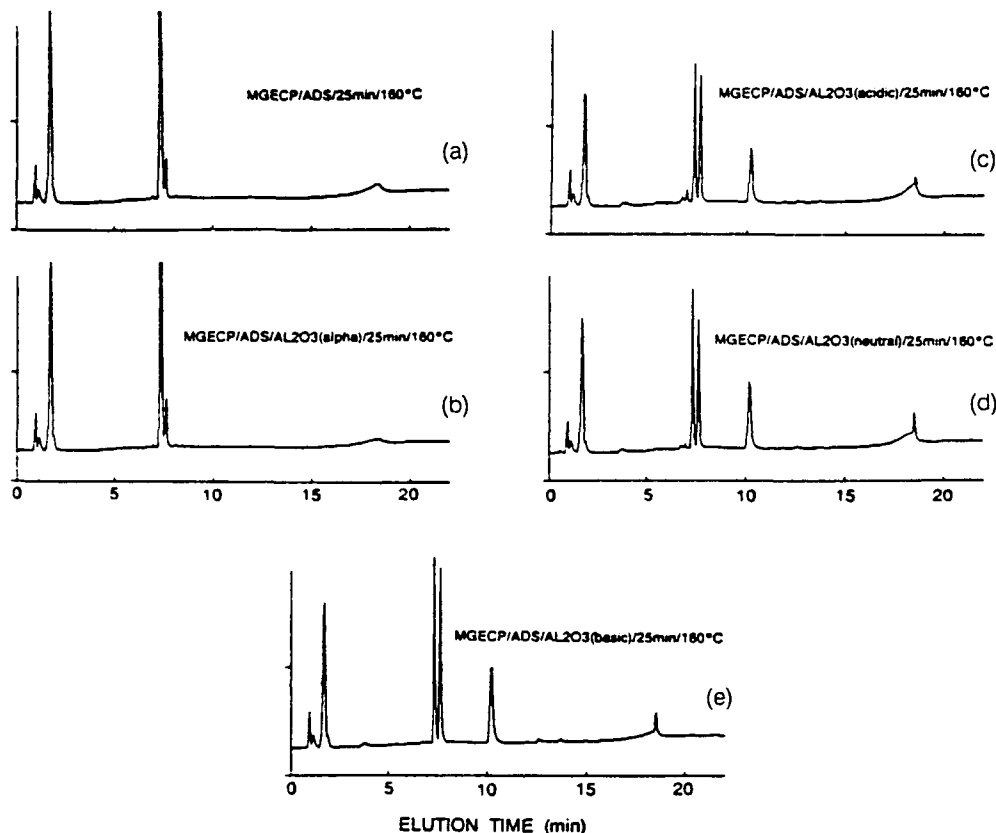
Figure 6. HPLC traces for a stoichiometric MGECP/ADS (a) unfilled, (b) 50 phr corundum filled, (c) 50 phr A/A filled, (d) 50 phr A/N filled, and (e) 50 phr A/B filled mixtures heated for 25 minutes at 160°C.
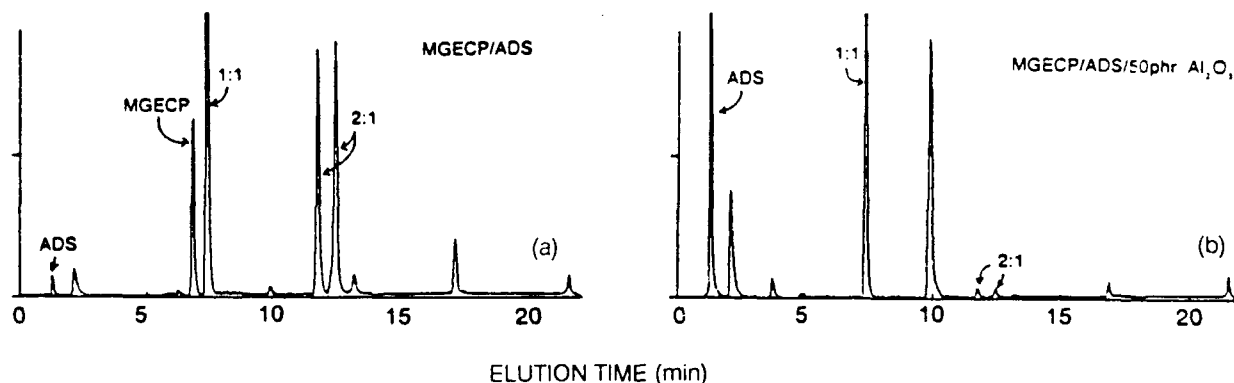
Figure 7. HPLC traces for a stoichiometric MGECP/ADS mixture (a) unfilled and (b) 50 phr A/N filled mixtures heated for 200 minutes at 180°C.

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Since only the epoxy appeared involved in this new route, mixtures were made using no curing agent. Unfilled MGECP and MGECP filled with 50 phr corundum, 50 phr A/A, 50 phr A/N, and 50 phr A/B aluminum oxides were heated for 50 min at 160°C and the HPLC traces shown in Figures 8a, 8b, 8c, 8d, and 8e, respectively. No reaction takes place in the unfilled and corundum filled MGECP as can be seen by examination of Figures 8a and 8b. Reaction does take place in the activated aluminum oxide filled samples with a reaction product having the same 10 min elution time as that observed for the activated aluminum oxide filled MGECP/ADS mixtures. Amine is clearly not required for the formation of this product.
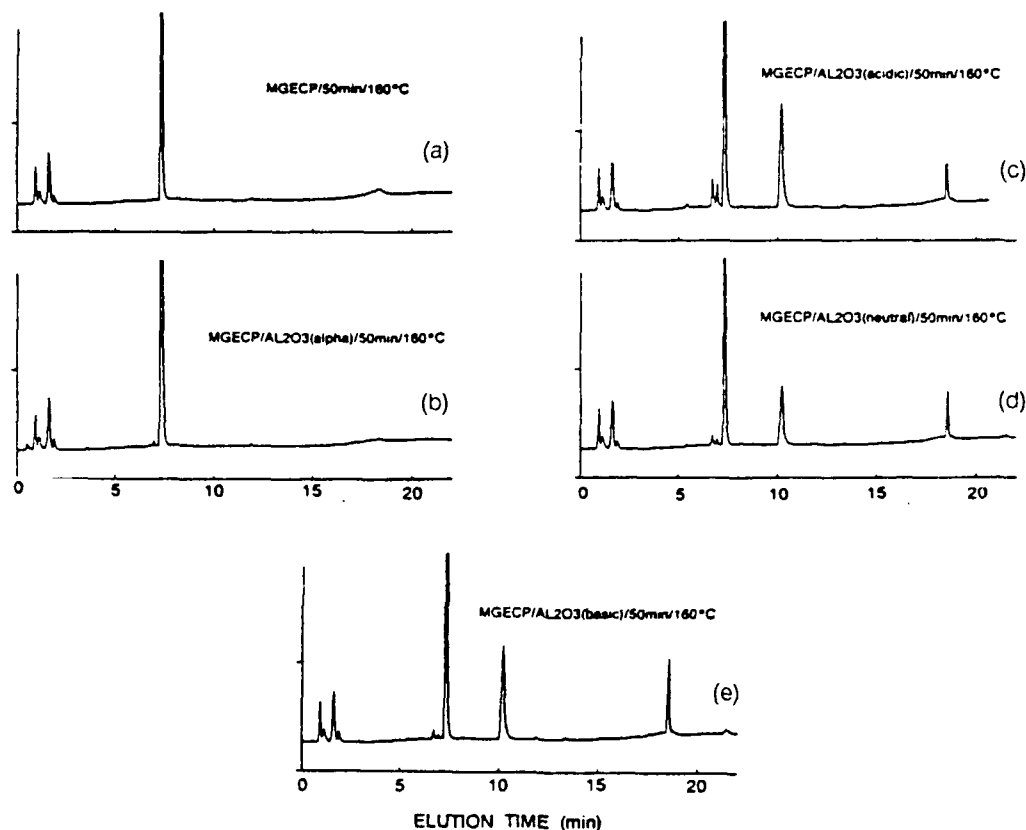
Figure 8. HPLC traces for (a) unfilled, (b) 50 phr corundum filled, (c) 50 phr A/A filled, (d) 50 phr A/N filled, and (e) 50 phr A/B filled MGECP heated for 50 minutes at 160°C.

A surprising result was the apparent lack of effect of the surface pH of the activated aluminum oxides. The HPLC traces for the systems containing the various activated aluminas in Figures 6 and 8 show no dependence of the product distributions on the surface pH. By contrast, Garton et al.[6] observed a strong dependence of the accelerated reactions on the pH of the carbon blacks in their study. This is planned to be investigated further.

Direct inspection probe mass spectrometry was carried out on the soluble material of the A/N filled MGECP reaction products. The parent ion of the HPLC 10 min elution product was shown to be a dimer of MGECP plus water. The activated aluminas thus appear to accelerate the dimerization and perhaps homopolymerization of the epoxy component.

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To test whether this same reaction occurs with a difunctional resin without an amine curing agent, a sample of 826 was heated both without and in the presence of 50 phr A/N aluminum oxide for 960 min at 160°C. These HPLC traces are shown in Figures 9a and 9b, respectively. Essentially no soluble reaction products were observed, the longer elution time peaks representing mostly the original oligomers in the 826. The homopolymerization process thus did not seem to extend to the difunctional resin. However, a careful mass balance revealed a significant amount of insoluble material remaining on the aluminum oxide.
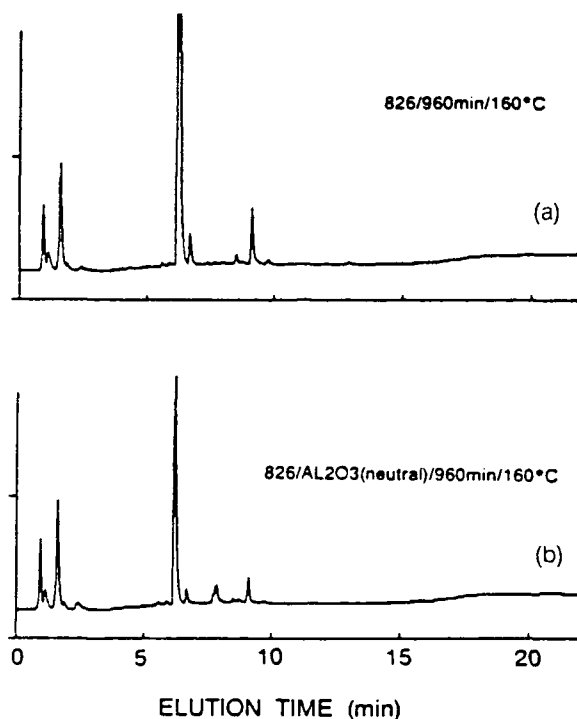
Figure 9. HPLC traces for (a) unfilled and (b) 50 phr A/N
filled 826 heated for 960 minutes at 160°C.

To determine the amount of insolubles produced by the various epoxy combinations, the solids were recovered from mixtures of MGECP/ADS heated for 25 min at 160°C, MGECP heated for 960 min at 160°C, and 826 heated for 960 min at 160°C all in the presence of 50 phr A/N aluminum oxide. Each was extracted with methylene chloride and vacuum dried at approximately 60°C, after which it was weighed and TGA performed in air to establish the organic content. These results are shown in Table 4 together with a value derived from the carbon content by elemental analysis. Good agreement between direct mass balance and TGA are shown with more than twice as much insoluble material observed for the difunctional 826 versus MGECP heated under the same conditions. Accelerated homopolymerization thus seems to be taking place with the 826 since this would rapidly lead to insoluble product formation which would remain on the aluminum oxide surface.

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Table 4. WEIGHT UPTAKE BY ACTIVATED A/N ALUMINA
RECOVERED FROM CURED RESIN SYSTEMS

Resin System	wt% by Mass	wt% by TGA	wt% by Elemental
MGECP/ADS (After 25 min at 160°C)	9	8	10
MGECP (After 960 min at 160°C)	10	11	-
826 (After 960 min at 160°C)	26	22	-

The A/N aluminum oxide from the MGECP/ADS mixture was further studied by FTR. Its spectrum, shown in Figure 10, contains absorption bands associated only with the MGECP moiety and the absence of the strong absorption band of the sulfone group of the ADS molecule at 1146 cm^{-1}. Elemental analysis of this same material indicated less than 5% of the expected sulfur if a stoichiometric product had remained on the surface. Pyrolysis mass spectrometry similarly showed no sulfur or nitrogen containing species to be present. These experiments demonstrate conclusively that the organic material remaining on the A/N aluminum oxide surface, even in the presence of the amine curing agent, is derived only from the epoxy component.
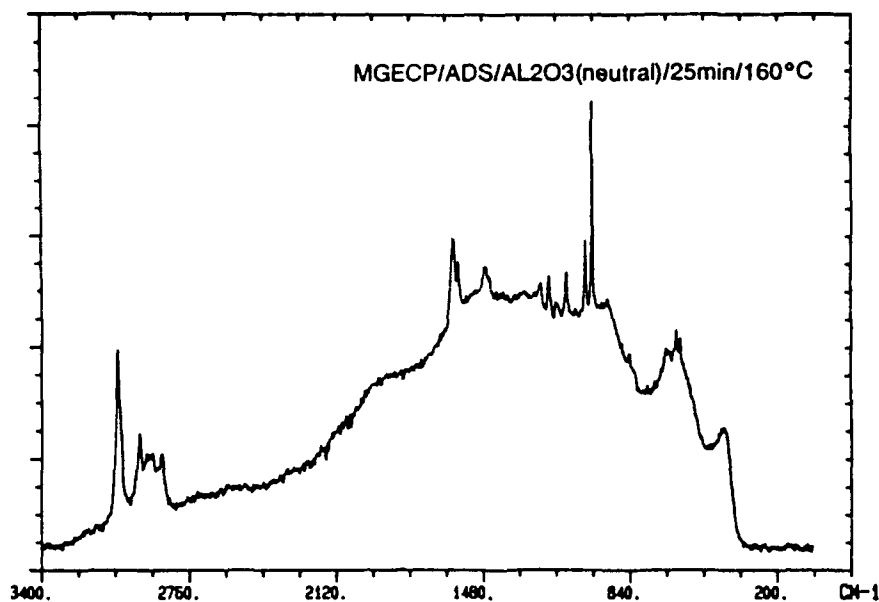
Figure 10. FTR spectra of the solids remaining after extraction of a stoichiometric MGECP/ADS mixture heated with 50 phr A/N for 25 minutes at 160°C.

CONCLUSIONS

DSC experiments on crosslinking epoxy systems show a much faster initial rate of reaction in the presence of an activated aluminum oxide which leads to a lower T_g material. Since total heat of reaction (and thus extent of reaction) remained a constant, a change in the relative rates of the reactions leading to network formation was implied. Preliminary HPLC results using a monofunctional amine and a monofunctional epoxy show faster amine addition

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to epoxy and a significantly increased rate of epoxy/epoxy reaction(s) in the presence of activated aluminum oxide. This homopolymerization leaves an excess of unreacted amine after complete epoxy conversion in a stoichiometric mixture. Water and/or hydroxyl groups are apparently important to this reaction pathway as evidenced by the inactivity of the crystalline corundum. A surprising result was the lack of effect of the surface pH of the activated aluminum oxides. Organic material was also observed to be bound to the activated aluminum oxide surfaces and consisted of epoxy derived material with little evidence of any incorporated amine.

Whereas previous studies have shown the bulk network structure of epoxy resins cured with aromatic amines to consist primarily of amine/epoxy addition products, this study has revealed that reactions involving only the epoxy become significant in the interphase. Homopolymerization and strong epoxy/surface interactions clearly result in an interphase whose structure differs markedly from that expected from the stoichiometric addition of amine to epoxy. While as yet unable to specify the precise structure of this material or the spacial product distribution, it can be readily imagined that perturbations of this sort in an actual bond would effect both strength and durability and must be reflected in the development of any predictive model. Studies are currently underway directed at each of these issues. Particular emphasis is being placed on the oxides resulting from typical surface preparation methods of aluminum for bonding.

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Key Words

Epoxy resins
Curing
Surface effects

Adherend surface effects on the amine cure of epoxy resins were investigated using finely divided aluminum oxide as high surface area models for aluminum. Calorimetric analysis of simplified crosslinking systems revealed significantly faster reactions which led to lower glass transition temperature materials for activated aluminum oxide filled samples. A mono-functional amine and epoxy were then utilized to obtain soluble reaction products amenable to molecular characterization. These studies similarly showed an increase in the rate of epoxy consumption in the presence of activated aluminum oxide which was attributed to both an increase in the rate of amine addition to epoxy, as well as to epoxy homopolymeriza-tion. The latter was not observed in the unfilled mixtures. Such changes in reaction mecha-nism at the adherend surface have implications for the strength and durability of actual adhesive bonds.